Microstructure and deformation mechanisms of a solid propellant using $^1$H NMR spectroscopy

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**Highlights**

- NMR $T_2$ relaxation time measures polymers segmental mobility.
- Comparing molecules, binders, and propellants determines the microstructural phases.
- 3 domains present in propellants: short, intermediate, and long relaxation times.
- When strained, polymer network stretched between fillers, sol fraction immobilized.

**Abstract**

Highly-filled elastomers such as solid propellants exhibit a complex nonlinear viscoelastic behavior. The microstructural origin of this behavior is difficult to ascertain with macroscopic observations. This article aims at identifying the deformation mechanisms of a solid propellant by measuring the change in segmental mobility with deformation. The novelty lies in the use of $^1$H Nuclear Magnetic Resonance (NMR) spectrometry to investigate the spin–spin relaxation times $T_2$ of a solid propellant. In addition, the effect of strain on $T_2$ is measured using a specific setup transmitting the loading of the tensile machine to the sample inside the NMR apparatus. We compare isolated components, unfilled binders, and solid propellants varying in composition according to a design of experiments. The design of experiments determines the influences of the filler fraction, the amount of curing agents, the plasticizer content, and the presence of filler–binder bonding agents, on the segmental mobilities. The propellant protons can be schematically divided into three segmental mobilities corresponding to distinct relaxation times. The short times correspond to the severely restricted segments situated around cross-links or fillers. The intermediate relaxation times correspond to segments of polymer chains linked at both ends. Finally, the long relaxation times correspond to the highly mobile segments of polymers (dangling ends) and to the plasticizer molecules. The influence of strain on the relaxation times shows that the polymer network is stretched between the fillers while part of the polymer in the sol fraction is immobilized. In addition, chain sliding on the filler surface and breaking of filler–binder links can occur.

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1. Introduction

Solid propellants are highly-filled elastomers, used for the propulsion of rocket launchers. The main physical characteristic of this class of materials is the large filler fraction, up to 88–90 wt% or 80% in volume, immersed in an elastomeric binder. Moreover, the binder in solid propellants is not fully cross-linked and incorporates a large quantity of plasticizer molecules. Consequently, the binder contains a significant amount of sol fraction, that is the fraction of the binder that can be extracted by swelling. The sol fraction is constituted of polymer chains and plasticizer and participate actively in the nonlinearity of the mechanical behavior [1–3]. Schematically, the propellant is composed of the fillers, the polymer network, and the sol fraction. The polymer network and the sol fraction constitute the binder.

The relations between the nonlinear mechanical behavior at the macroscopic scale and the microstructure at the scale of the fillers or the polymer chains have been explored [1–6]. However, direct experimental evidence of the physical mechanisms of deformation at the scale of the polymer network is difficult to obtain. In order to reach this goal, we precisely explore the deformation mechanisms in the binder of solid propellants by measuring the change in segmental mobility with deformation using nuclear magnetic spectrometry. The novelty of the approach lies in the application of this method to measure and understand the influence of strain on the segmental mobility. For solid propellants, this type of measurement has only been performed on an isolated binder in [7].

The $^1H$ Nuclear Magnetic Resonance (NMR) $T_2$ relaxometry directly measures the transversal spin relaxation of the protons of the polymer chain, without modifications of or additions to the material under scrutiny [8,9]. The spin relaxation takes place at an atomic scale and is influenced by the local environment of each proton [10]. As a consequence, the transversal or spin–spin relaxation time $T_2$ of the spins varies according to the mobility of the molecular segment on which they are situated. Therefore, the $^1H$ NMR $T_2$ relaxometry enables the measure of segmental mobility [9]. The measurement commonly results in the continuous spectrum of relaxation times for the protons in the material. If the material is considered to be heterogeneous [11], i.e. made of different type of segments or phases, then commonly the continuous spectrum is discretized in a series of different systems each associated with segments. The corresponding discrete relaxation times are then the average time of each mobility. The relative contribution of each segment type to the total relaxation spectrum is proportional to the quantity of protons on these types of segments [10].

Previous investigations of filled and unfilled elastomers showed that the introduction of fillers creates a microstructure containing a large range of segmental mobility [12–18]. The segments of the polymer network in the bulk of the binder present a higher mobility than the same unfilled elastomer [12–14,19,20]. Topological constraints created by the fillers reduce the mobility of all the polymer segments [15]. In the case of reinforcing fillers, a highly-constrained phase is measured and corresponds to immobilized polymer segments on the surface of the fillers [10]. Finally, free polymer molecules participate in the high mobility fraction [17].

The influence of deformation on segmental dynamics has been explored through $T_2$ relaxometry experiments on strained unfilled and filled elastomers [21–26]. The overall conclusion of the studies is that an increasing tensile strain emphasizes the anisotropy of the network causing a decrease of the relaxation time [27–31]. In addition, the sol fraction interact with network chains and orient according to network deformation [32–34].

2. Materials and methods

2.1. Materials

Three categories of materials have been tested: (i) hydroxyl-terminated polybutadiene (HTPB) polymer chains and plasticizer molecules, to allow the comparison with other systems, (ii) two binders corresponding to an HTPB polymer network, without and with plasticizers, denoted as 1 and 2, respectively, and (iii) a large number of propellant systems.

The propellant systems have as fillers ammonium perchlorate and aluminum, with sizes 20–200 μm and 5 μm, respectively. Filler–binder bonding agents (FBBA) are introduced to prevent or delay dewetting by linking chemically to the polymer chains in the binder and to the filler surface [35]. The exact synthesis of the FBBA molecules is confidential and will therefore not be described. More details on the FBBA are provided in [6] but are not essential to this study.

The binder is constituted of HTPB prepolymer cured with a methylene diicyclopentadiene (MDCI). The ratio of the quantity of isocyanate functions NCO with respect to the quantity of hydroxyl functions OH in the introduced polymer determines the NCO/OH ratio. In short, the NCO/OH ratio is a measure of the relative quantity of curing agents. The plasticizer introduced is diocyl azelate (DOZ) molecules.

The materials are thermally cured for 2 weeks at 50 °C. The propellants numbered 0 to 21 (Table 1) correspond to a design of experiment (DoE) allowing us to determine the influence of four composition factors (the filler fraction, the FBBA, the NCO/OH ratio, and the plasticizer content) on the properties of an HTPB-based solid propellant. The principles of building the DoE have been detailed elsewhere [1,6].

2.2. $^1H$ NMR spectroscopy

2.2.1. CPMG sequence

All $^1H$ NMR $T_2$ relaxation measurements were conducted in the solid at room temperature, i.e. above the glass transition of all the tested materials, using a low resolution DIASPEC apparatus (ARTEC systems, frequency 19.623 MHz). The pulse sequence employed for the relaxation experiments was the standard Hahn-echo or CPMG [36,37] two pulse sequence conducted on resonance $90 \text{deg} - [\pi - 180 \text{deg} - \tau_n] - \text{echo}$. The CPMG sequence does not avoid the “dead time” of the NMR spectrometer, in this case 20 μs, and thus, focuses on the relatively long relaxation times [10]. The protons of the material with a very low mobility such as those in the fillers are not measured. The length of the 90 and 180 pulse is 7.5 and 15 μs, respectively. $\tau$ is equal to 55 μs and $n$ is chosen between 700 and 1000 to observe the full decay. Finally, to limit the influence of the noise, the sequence is repeated between 32 and 64 times at time intervals of 1 s.

2.2.2. Strained NMR setup

To study the influence of mechanical deformation on the segmental mobility of the propellant, a setup combining the NMR apparatus and an INSTRON tensile machine is developed. The NMR apparatus is placed on the base of the tensile machine (Fig. 1(a)). The stresses are transmitted through a frame made of steel for the exterior parts and PEEK (PolyEtherEtherKetone) for the interior parts (Fig. 1). This polymer has no influence on the NMR results because its protons exhibit a very low mobility [38]. In addition, PEEK provides a high mechanical strength to the set up. Several teams have built similar setups dedicated to NMR spectrometry of strained specimens [21,28,38–41].
For each material, a rectangular specimen of dimensions 50 × 10 × 5 mm is glued to PEEK grips, placed in the NMR apparatus and fastened using the PEEK grips to the tensile machine. The detection coil in the apparatus exhibits a height of 20 mm, which determines the measurement window. The mechanical strain, applied at a strain rate of 0.1%/s, reaches up to 20%, the maximal value depending on the elongation at failure of each material. If the maximum elongation is lower than 8%, the specimen is tested every 1% of strain, otherwise, every 2% of strain. As a precaution, in order to reach a mechanical quasi-equilibrium state, the specimen is left to relax between 5 and 30 min before measuring the segmental mobility.

2.2.3. Signal processing

The NMR test provides the echo height \( M(t) \) as a function of time \( t \). Because the material quantity seen by the NMR apparatus varies during stretching – one part will exit the observation window (Fig. 1), the height of the echo is normalized so that the quantity of material in the apparatus does not influence the results. Accordingly, the materials can be quantitatively compared to each other.

This raw data is deconvoluted by an inverse Laplace transform:

\[
\frac{M(t)}{M(0)} = \sum_{i=1}^{80} A_i \exp \left( -\frac{t}{T_{2i}} \right),
\]

where \( M(0) \) is the height of the echo at the time \( t = 0 \). \( T_{2i} \) is the disctretized spectrum of the relaxation times \( T_{2} \), and \( A_i \) the amplitude associated with each \( T_{2i} \). An example of the result can be seen in Fig. 2.

This discretized spectrum makes it uneasy to quantitatively compare the materials of the DoE, which is necessary to determine the influence of each factor. From this first processing, we chose to represent the behavior of the propellants with 3 relaxation times. The relaxation times \( T_{2} \) and the associated fractions of the material \( f_i \) are determined from the normalized echo height \( M(t)/M(0) \) using Eq. (2).

\[
\frac{M(t)}{M(0)} = f_s e^{-\frac{t}{\tau_s}} + f_m e^{-\frac{t}{\tau_m}} + f_l e^{-\frac{t}{\tau_l}},
\]

where \( s, m, \) and \( l \) stand for short, medium, and long, respectively, and \( f_s + f_m + f_l = 1 \). The parameters \( \tau_s, \tau_m, \tau_l, T_{2s}, T_{2m}, T_{2l} \), and \( T_{2s} \) have been identified from the NMR measurements using a Levenberg–Marquardt algorithm in Mathematica®. An example of the raw signal and its decomposition into three exponential terms is presented in Fig. 3. A correlation coefficient higher than 0.96 is obtained for all the fitted data.

In order to quantify the effective mechanical strain imposed to the specimen, we assume incompressibility and the rough approximation of the Gaussian network theory [42]. As a consequence, the effective strain \( \lambda' \) is defined as:

\[
\lambda' = \frac{\lambda^2 - 1}{\lambda}
\]

where \( \lambda \) is the imposed tensile stretch. In the studied range, \( \lambda' \) is proportional to \( \lambda \). The use of this variable allows to take into account the effect of large deformations and to compare with previous studies [21,28,40]. We note that \( \lambda' \) does not represent the effective strain at the molecular scale, which would depend on multiple factors and most prominently on strain amplification.

The influence of the effective strain on the relaxation times \( T_{2i} \) and associated fractions \( f_i \) is quantified by \( \partial T_{2i}/\partial \lambda' \) and \( \partial f_i/\partial \lambda' \), respectively (Fig. 4).

2.3. DoE analysis

Finally, as presented in details in [1,6], the DoE method is applied to the 12 responses: \( T_{2s}, T_{2m}, T_{2l}, f_s, f_m, f_l \) and their derivatives with respect to the effective strain \( \lambda' \), \( \partial T_{2s}/\partial \lambda' \), \( \partial T_{2m}/\partial \lambda' \), \( \partial T_{2l}/\partial \lambda' \), \( \partial f_s/\partial \lambda' \), \( \partial f_m/\partial \lambda' \), and \( \partial f_l/\partial \lambda' \), using the Design-Expert® software. A model with n coefficients can only be investigated with a DoE consisting of at least n runs. According to the number of factors chosen and the number of materials manufactured, the possible models are: mean value, linear, first order interactions,
or quadratic. The unknown constants of the model are obtained by optimization on the experimental results. An analysis of variance determines the model form best representing the results while taking into account the least number of terms. A second analysis

![Image of stretched NMR set up](image_url)

**Fig. 1.** NMR set up in the tensile machine.

**Fig. 2.** Example of the inverse Laplace transform applied to the magnetization decay of the propellant 'Ref'.

**Fig. 3.** Magnetization decay of the propellant 'Ref' and its decomposition according to Eq. (2).

**Fig. 4.** Relaxation times and fractions of the propellant 'Ref' according to strain.
of variance is performed on the chosen model form to eliminate the terms corresponding to non influential factors or interactions (p-value < 0.05).

The final model represents the response according to the factors of the DoE, here variables of material composition. The good fit of the model is evaluated by the adjusted correlation coefficient $R^2_{adj}$ [43], which takes into account the number of terms in the model.

3. Results and discussion

3.1. Fit of the DoE models

Table 2 specifies the $R^2_{adj}$ for each parameter $p$ and its derivative with respect to the effective strain $\partial p_{r}$.

The $R^2_{adj}(\partial p_{r})$ are, as expected, lower than $R^2_{adj}(p)$. However, only $R^2_{adj}(\partial f_{s})$ and $R^2_{adj}(\partial T_{2m})$ show that the obtained models unsatisfyingly fit the experimental data. The lack of fit originates from two factors. First, the derivatives are of the order of $10^{-2}$ for the fractions $f_{s}$ and of the order of $10^{-1}$ or 1 for the times $T_{2l}$. The influence of noise on the experimental data is then statistically significant during the DoE processing. Second, the used CPMG sequence focuses on the relatively long relaxation times. As the material is stretched, the protons in the low mobility segments become even more constrained and their relaxation time might become too short to be measured with this sequence. The low correlation between the slope of $f_{s}$ and the model results from this technical limit.

3.2. Relaxation of the microstructure

In short, the microstructure of a solid propellant can be schematically decomposed into the fillers, the polymer network and the sol fraction, which contains the sol polymer and plasticizer molecules [6,1].

3.2.1. The fillers

Fig. 5 compares the relaxation times of the HTPB molecules, the plasticizer molecules, binder 1, binder 2, and a solid propellant. The comparison of binder 2 and the propellant ‘Ref’ shows that introducing fillers leads to a decrease of 0.3 and 16 ms of the times $T_{2s}$ and $T_{2m}$, i.e. 30.6% and 37.9% respectively. $T_{2m}$ remains constant.

The DoE provides further information on the influence of the filler fraction on the relaxation times (Fig. 6) and their associated fractions. The DoE models indicate that the filler fraction has no influence on the fractions $f_{s}$, $f_{m}$, and $f_{l}$. Again, $T_{2l}$ decreases while $T_{2m}$ remains constant with an increase in filler fraction. According to the DoE models, $T_{2l}$ does not depend on the filler fraction which is opposite to what is observed in the direct comparison of a binder and a propellant. However, $T_{2s}$ depends on the FBBA.

Both the binder 2 and the propellant ‘Ref’ exhibit a fraction of material relaxing at short times $T_{2s}$. As a consequence, this time does not correspond to the protons close to the fillers only. Notwithstanding, the protons close to the fillers have a significantly reduced mobility, notably because of the action of FBBA. This explains the decrease of the time $T_{2s}$ as an average when fillers are introduced into the material and when the filler fraction increases.

Although the plasticizer content of the propellant ‘Ref’ is higher than the one of the plasticized binder, the time $T_{2m}$ of the propellant is still shorter. Studying a filled PDMS elastomer, Litvinov and Zhdanov [15] suggested that the topological constraint, created by fillers, limits the movements of the chains. Therefore, the introduction of fillers results in a decrease of all relaxation times in the material.

Although the filler fraction has no effect on the model obtained for $T_{2s}$, this is the only model taking into account the influence of the FBBA. The interaction between the filler fraction and the presence of FBBA makes it difficult to distinguish their specific influence. As discussed previously [6], the FBBA creates a rigid layer of polymer around the fillers that increases the effective filler

![Fig. 5. Comparison of the relaxation times of the molecules, the binders, and the propellant ‘Ref’.

![Fig. 6. Influence of the filler fraction and the FBBA on the relaxation times $T_{2}$ (NCO/ OH = 0.95, plasticizer content = 20%wt of the binder).](image-url)
volume, and hence the influence of the filler fraction on the studied property. In this case, the presence of FBBA decreases significantly $T_{2l}$, hence reducing the mobility of the less constrained segments.

### 3.2.2. The polymer network

Comparing HTPB chains and the binder 1 (Fig. 5), the creation of a network reduces the unique relaxation time of the free HTPB chains. Noticeably, an unfilled polymer network presents two relaxation times different by one order of magnitude and corresponding to $T_{2m}$ and $T_{2m}$. Moreover, $f_l$ decreases and $f_m$ increases with an increase in NCO/OH ratio, while $f_m$ remains constant (Fig. 7(a)). The constance of $f_m$ results more likely from the shift in mobilities of chain fragments from $f_l$ to $f_m$ and from $f_m$ to $f_s$, than from the fact that the change in NCO/OH ratio does not affect the protons of $f_m$. Finally, all the relaxation times $T_2$ decrease when NCO/OH ratio increases (Fig. 7(b)).

The results prove that the various segments of the network do not exhibit an identical mobility: the constraint is larger on the protons close to a cross-link than on the ones situated further away. As a consequence, the short times $T_{2l}$ correspond to protons on segments close to the cross-links and $f_s$ increases with an increasing NCO/OH ratio.

Under the assumption that $f_m$ remains constant due to the transfer of protons from $f_l$ to $f_m$ and from $f_m$ to $f_s$, $f_m$ corresponds to the protons of chains constrained by a cross-link but on segments situated further away from the cross-links than the protons of $f_s$. These segments can be located in the network or in the high molar mass sol polymer fraction that appears at high NCO/OH ratios [1].

An increase in NCO/OH ratio decreases the sol polymer fraction [1] and the fraction of material $f_l$ corresponding to long relaxation times (Fig. 7(b)). Protons of small free polymer chains are then logically attributed to $f_s$. The decrease of $T_{2l}$ with increasing NCO/OH ratio shows that the relaxation of sol polymer chains that are not directly constrained by a cross-link is still disturbed by an increase in cross-link density. The segmental mobility of the free molecules is then assumed to depend on the mesh size.

### 3.2.3. The sol fraction

Plasticizer molecules are by definition low molar mass molecules, contrary to polymer macromolecules. The mobility of plasticizers and the associated relaxation time $T_2$ are high. Indeed, the measured relaxation time for plasticizer molecules is $257 \text{ ms}$ (Fig. 5). Thus, the relaxation of the protons of the plasticizer is identified with the third exponential term of Eq. (2) only, i.e. $f_s e^{-T_{2s}}$.

Comparing the relaxation times $T_2$ for the plasticizer molecules, the binder 2, and the propellant 'Ref' shows a decrease of about $150 \text{ ms}$ in the times $T_{2l}$ (Fig. 5). A simple averaging of the relaxation times in the $f_l$ fraction cannot justify such a decrease. As a result, the mobility of plasticizer molecules is diminished by the neighboring polymer macromolecules; namely the polymer chains have an anti-plasticizer effect on the plasticizer. This decrease of plasticizer mobility has been observed for various filled elastomers [44] and proves that their is a physical interaction between the plasticizer molecules and the polymer chains.

The change in plasticizer content artificially influences the distribution of protons. An increase in plasticizer content increases the fraction $f_l$ attributed to mobile segments. Since the measured quantity of material is normalized, the fractions $f_s$ and $f_m$ necessarily decrease. As a consequence, the influence of the plasticizer content on the fractions $f$ is not studied.

Fig. 7(b) shows that the increase of the plasticizer content does not influence $T_{2l}$ but increases $T_{2m}$ and $T_{2l}$.

The increase is particularly important for $T_{2l}$. Again, since an increase in plasticizer content increases the fraction $f_l$ only, it also increases $T_{2l}$ averaged over the material. This averaging effect on $T_{2l}$ cannot be distinguished from the increase of the mobility of polymer chains due to an actual plasticizing effect. On the contrary, the increase in $T_{2m}$ is the direct result of the increase of the mobility of the polymer segments by plasticizing.

As a conclusion, the evolution of the relaxation times according to the plasticizer content indicates an increase of the mobility of protons on polymer segments that are not directly linked to a filler surface or a cross-link. To summarize, the measurements allow for the determination of the location of the relaxation times into the microstructure (Fig. 8). Three types of segments with distinct relaxation times are observed:
Fig. 8. Scheme of the distribution of relaxation times $T_2$ in the microstructure.

- $f_s$ corresponds to the protons of the segments close to the filler surface or to a cross-link.
- $f_m$ corresponds to the protons of the segments of the polymer chain not directly linked to a cross-link. These segments can be located in the network or the sol fraction.
- $f_l$ corresponds to the protons of the plasticizer molecules and segments of the low molar mass sol polymer. Protons from dangling ends are also attributed to long relaxation times $T_2$.

3.3. Micromechanisms during deformation

$\delta f_{s,\ast}$ is positive whereas $\delta f_{m,\ast}$ is negative over the whole studied range (Figs. 9 and 10). Moreover, $\delta f_{l,\ast}$ is positive at low filler fractions and negative otherwise. $\delta f_{l,\ast}$ decreases towards the negative values when FBBA are introduced.

The fraction of low mobility protons increases, while the fractions of medium and high mobility protons decrease. Therefore, stretching the material leads to at least two phenomena: a transfer of protons from $f_m$ to $f_s$ and a transfer of protons from $f_l$ to $f_m$. Under particular conditions, a third mechanism appears: a transfer of protons from $f_l$ to $f_s$.

$\delta T_{2,\ast}$ is negative and $\delta T_{2,\ast}$ is positive over the tested range. However, as the time $T_{2,\ast}$ decreases, the limit of measurement of the apparatus is reached and the measurement is deemed unreliable. $\delta T_{2,\ast}$ is close to zero and is positive or negative according to the levels of the filler fraction, the NCO/OH ratio, and the presence or absence of FBBA.

The average mobility $T_{2,\ast}$ of the protons in $f_s$ logically decreases when the material is stretched. On the contrary, the average time $T_{2,\ast}$ of the protons in $f_l$ increases with strain. Indeed, the application of the mechanical strain constrains most of the protons in the material, including part of the protons in $f_s$. If those protons were still contributing to $f_s$ after stretching, $T_{2,\ast}$ would decrease. We assume that these protons are transferred from $f_l$ to $f_m$. Only the protons able to accommodate the deformation are contributing to $f_s$ after stretching. They belong to highly mobile molecules such as the plasticizers or the low molar mass sol polymer chains and present high relaxation times $T_{2,\ast}$. As a consequence, the average time $T_{2,\ast}$ increases with strain.

To determine what mechanism corresponds to the observed transfer of protons from one mobility to another, we detail the influence of each factor on $\delta f_{s,\ast}$ and $\delta T_{2,\ast}$.

3.3.1. Transfer from $f_m$ to $f_s$

The filler fraction is the most influential factor on $\delta f_{s,\ast}$. $\delta f_{s,\ast}$ increases strongly with the filler fraction while the negative $\delta f_{m,\ast}$ and $\delta f_{l,\ast}$ decrease strongly when the filler fraction increases. Moreover, $\delta f_{s,\ast}$ and $\delta f_{m,\ast}$ decrease with an increasing NCO/OH ratio. Finally, the negative $\delta T_{2m,\ast}$ decreases strongly when the NCO/OH ratio increases.

Fig. 9. Influence of the filler fraction and the FBBA on the evolution of the relaxation with mechanical strain (NCO/OH = 0.95, plasticizer content = 20%wt of the binder).

First, the rise of the filler fraction leads to a phenomenon known as strain amplification [45], which denotes that the local strain in the binder is higher than the imposed macroscopic strain and arises when rigid fillers are introduced in the binder.

Second, the fillers rearrange with the deformation and constrain the binder. The heterogeneous distribution of stresses in the microstructure leads to parts of the binder being highly stretched while others are compressed in between fillers [46,47]. Depending on the NCO/OH ratio, the network reaches its finite extensibility for a specific local strain. When the NCO/OH ratio increases, the cross-link density increases and the finite extensibility of the network decreases. Segments of the polymer network, previously attributed to $f_m$, become less mobile. Their relaxation time $T_{2m}$ decreases until they transfer to $f_s$. 
3.3.2. Transfer from $f_l$ to $f_m$

When the filler fraction increases, $\partial f_{1^*}$ becomes negative and $\partial T_{2m}$ becomes positive. An increase in the NCO/OH ratio or the introduction of FBBA decreases $\partial T_{2m}$. The increase in NCO/OH leads to a decrease of the network mesh size [1] and hence a decrease in the volume available to the high mobility protons of the free molecules or dangling ends.

When the filler fraction is high, the volume taken up by the fillers is large. The presence of FBBA increases the filler effective volume and the concentration of cross-links in the vicinity of the fillers [6]. Consequently, protons attributed to $f_l$ are constrained in the stretched polymer network, their relaxation time $T_{2l}$ decreases until they transfer to the fraction $f_m$. In turn, the average measured $T_{2m}$ increases. This phenomenon also explains the weakness of $\partial T_{2m}$. 

3.3.3. Increase in $f_l$

$\partial f_{1^*}$ is positive when the filler fraction is small and is decreased towards the negative values by the introduction of FBBA. In addition, $\partial T_{2m}$ decreases when FBBA are added. The increase of $f_l$ with deformation implies a different mechanism, involving the removal rather than the creation of constraints.

At a low filler fraction, the volume available to the network and the sol fraction is high. In addition, the distance between fillers is increased. Finally, the influence of the FBBA on this particular effect shows that the mechanism is located at the interface between the fillers and the binder.

Two mechanisms are envisioned. First, the rupture of weak filler–binder links [48] with deformation creates dangling ends and/or sol polymer molecules. As a consequence, protons from $f_l$ are transferred into $f_m$ or directly into $f_l$.

Second, Dannenberg et al. [49] suggested that the polymer chains slide on the filler surface to accommodate deformation. This molecular rearrangements diminish internal constraints, distribute the stresses more homogeneously, and prevents the local decrease of network mesh size by stretching. The mechanism liberates sol polymer molecules that were constrained in the network either by topological or physical constraints. Therefore, protons from $f_m$ are transferred to $f_l$.

4. Conclusion

The objective of this article is to identify the deformation mechanisms of a solid propellant by measuring the change in segmental mobility with deformation. The novelty lies in the investigation of the spin–spin relaxation times $T_2$ of a HTPB-based solid propellant by comparing isolated components, unfilled binders, and a series of solid propellants varying in composition according to a DoE.

The first result reveals that the protons in a solid propellant can be schematically divided into three segmental mobilities corresponding to three distinct relaxation times. The short times correspond to the highly restricted segments situated around cross-links or fillers. The intermediate relaxation times correspond to segments of polymer chains linked at both ends, participating to the polymer network or to the sol fraction. Finally, the long relaxation times correspond to the highly mobile segments of polymers (dangling ends) and to the plasticizer molecules.

The influence of the deformation is determined via a specific setup where the loading of the tensile machine is transmitted to the sample inside the NMR apparatus. The influence of the factors of the DoE is less visible on the derivatives of the parameters with respect to strain than on the original parameters. However, the evolution of the fraction of material corresponding to each mobility (short, medium, and long times) as well as the evolution of the relaxation times with strain suggest four mechanisms:

- The polymer network is strained in between the fillers, creating high stress bands in the microstructure and allowing the polymer chains to reach their finite extensibility. Thus, the segments of the polymer chains of the network show a decreased mobility.
- Part of the polymer in the sol fraction is immobilized in the stretched network and between fillers that are rearranging according to the imposed strain.
- In the absence of FBBA, chain sliding on the filler surface is envisioned to allow for a molecular rearrangement of the network, which leads to a more homogeneous distribution of the stress and can remove constraints on segments.
– Finally, the imposed strain might break weak filler–binder links and create dangling chains. This mechanism would also remove constraints on specific segments.

Although the presence of plasticizers limited the analysis of the highly mobile fraction, this study demonstrates the potential of the \(^1\)H NMR technique to study the complex microstructure of solid propellants. Future analyses and experiments on this problem should include a more detailed comparison of binders and propellants without plasticizers in order to specify the interaction between sol and network polymer chains.

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